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S. A. Asher and G. Pan

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University of Pittsburgh  
Department of Chemistry  
Pittsburgh, PA

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## CRYSTALLINE COLLOIDAL ARRAY OPTICAL SWITCHING DEVICES

S. A. ASHER and GUISHENG PAN

*Department of Chemistry  
University of Pittsburgh  
Pittsburgh, PA 15260*

### 1. Introduction

Crystalline colloidal arrays are mesoscopically periodic materials which efficiently diffract light meeting the Bragg condition.<sup>1-4</sup> These materials consist of arrays of colloidal particles which self assemble in solution into BCC or FCC crystalline arrays<sup>5</sup> (Fig. 1). This self assembly is the result of electrostatic repulsions between colloidal particles, each of which have significant numbers of charged surface functional groups. We have concentrated on the development of crystalline colloidal arrays<sup>6-9</sup> which, diffract light in the visible spectral region, and have generally utilized colloidal particles of ca. 100 nm diameter. These particles have thousands of charges, which result from the ionization of sulfonate groups attached to the particle surface. The nearest neighbor distances are ca. 200 nm.

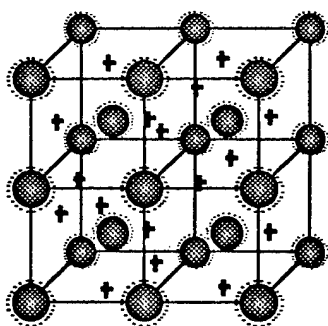


Fig. 1 Crystalline colloidal array composed of a BCC array of negatively charged colloidal particles. The colloidal particle charge derives from ionized surface sulfonate groups. The counterions in the surrounding medium keep the system neutral.

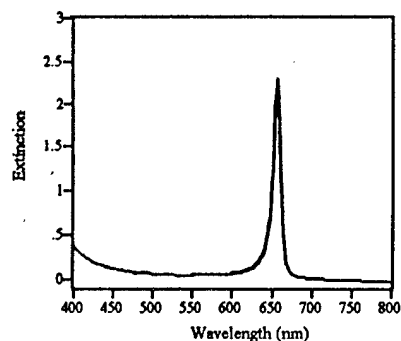


Fig. 2 Transmission spectrum of a 1.0 mm thick crystalline colloidal array formed from 131 nm diameter poly(heptafluorobutyl methacrylate) particles. The particle volume fraction was 6.13%.

These BCC or FCC cubic arrays are well ordered and the arrays strongly diffract light in the visible spectral region (Fig. 2). We earlier demonstrated<sup>2,3</sup> the use of these devices as optical filters. We more recently developed methods<sup>10</sup> to solidify and rigidize these arrays by imbedding the cubic lattice in a hydrogel polyacrylamide lattice (Fig. 3). This system can be prepared such that the acrylamide and the colloidal array occupy a small percent of the sample volume; most of the volume consists of water. The medium surrounding the spheres can be modified since other solvents can be diffused around the array to replace the water. Although the hydrogel linked crystalline colloidal array shows swelling and shrinkage as the solvent medium is changed, the array ordering is maintained. Films of this array can be prepared where the 110 plane of the BCC lattice is well oriented and parallel to the surface. The 110 planes of the periodic colloidal structure in the film will strongly diffract light meeting the Bragg condition.

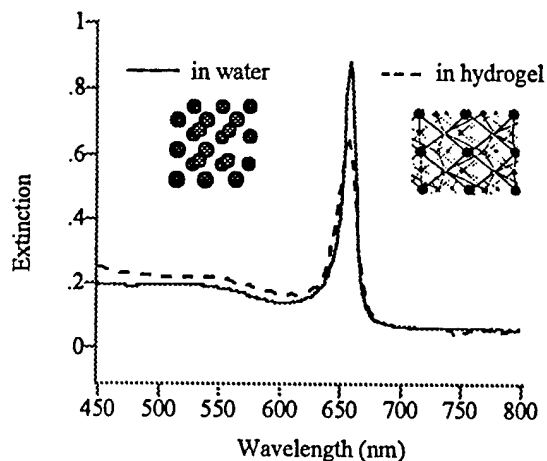


Fig. 3 Transmission spectra of 155 nm diameter poly(heptafluorobutyl methacrylate) crystalline colloidal array before and after solidification in a polyacrylamide hydrogel matrix.

We earlier suggested that we could build nonlinear optical switching materials<sup>11-16</sup> by creating an array consisting of polymer spheres containing dye. We would adjust the composition of the medium such that the real part of the refractive index of the spheres was identical to that of the medium.<sup>17</sup> Thus, the array would not diffract light which meets the Bragg condition. However, at high incident light intensities, significant heating would occur within the colloidal particles, the temperature would increase, the refractive index would decrease, and the array would "pop up" to diffract light. We calculated that this onset of diffraction could occur within 5 nsec with pulsed laser sources.<sup>11</sup>

We demonstrate here the first observation of this nonlinear diffraction phenomenon.

## 2. Experimental

Monodisperse colloidal particles of a highly fluorinated monomer were prepared with a diameter of 138 nm. These spheres were copolymerized with an acylated Oil Blue N polymerizable dye. The refractive index of these spheres was 1.393, which is lower than that of any monodisperse colloids previously reported. The synthetic methodology will be reported elsewhere.

These colloids self assembled into a crystalline colloidal array which was polymerized within an acrylamide hydrogel. Dimethylsulfoxide was added to the mainly aqueous medium in order to adjust the medium refractive index to the appropriate value either slightly above or slightly below that of the colloidal particles.

Diffraction from the array was monitored using the experimental apparatus shown in Figure 4. The 532 nm pump beam derived from a Coherent Radiation Infinity YAG laser. The probe beam derived from a dye laser pumped by this YAG. The pump and the probe beams were of ca. 3 nsec duration, and were made coincident on the sample, but the probe beam was adjusted temporally such that it was delayed by ca. 3 nsec compared to the pump beam. The relative angle of the sample to the pump beam was adjusted such that the Bragg condition was met. If the refractive index were exactly matched no diffraction should be observed in the absence of the pump beam. If the refractive index of the colloidal particles were adjusted to be slightly greater or less than that of the medium, a very small fraction of the probe beam will diffract.

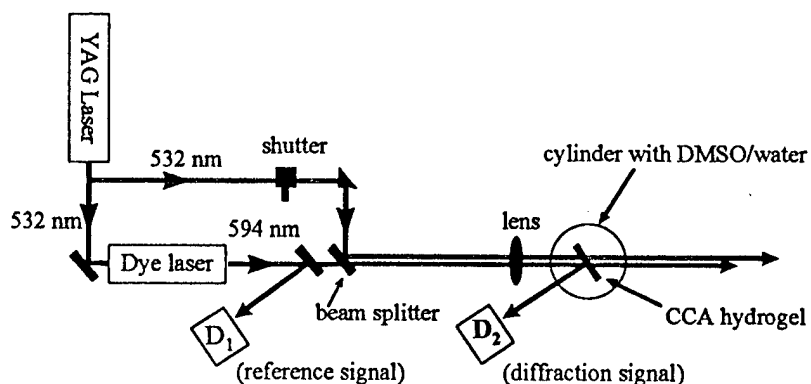


Fig. 4 Schematic of the experimental apparatus for optical nonlinear diffraction measurements.

## 3. Results and Discussion

Figure 5 shows the extinction spectrum of this dyed crystalline colloidal array hydrogel film measured at normal incident. The broad band centered around 520 nm

results from dye absorption from the colloidal particles. The peak at ca. 640 nm results from Bragg diffraction by the BCC 110 plane.

The film was oriented such that its normal made an angle of ca.  $15^\circ$  relative to the incident beam, so that light at the dye laser output at 594 nm would be diffracted. Figure 6 shows two measurements where the medium has a refractive index of either 1.4045 or 1.3610, which is either above or below the sphere refractive index, respectively. Figure 6 plots the relative value of the diffracted light intensity at various pump energy values compared to the value in the absence of the pump laser.

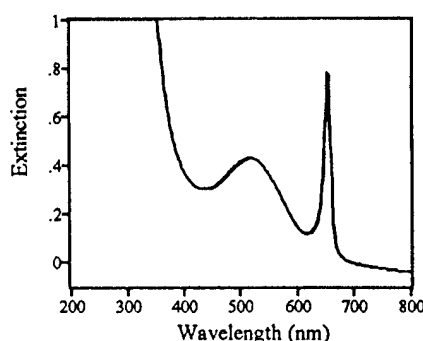


Fig. 5 Transmission spectrum of 138 nm dyed poly(heptafluorobutyl methacrylate) crystalline colloidal array solidified in a polyacrylamide hydrogel matrix.

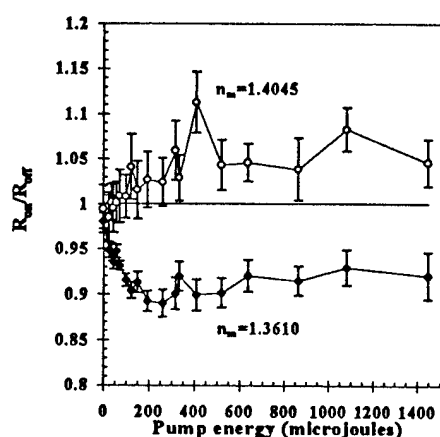


Fig. 6 Pump beam energy dependence of Bragg diffraction intensity. The relative value of Bragg diffraction intensities ( $R_{on}/R_{off}$ ) were monitored at various pump beam energies.

As expected, if the colloid refractive index is below the medium, heating by the incident beam lowers the colloid refractive index and the diffracted intensity increases. In contrast, if the colloid refractive index is above that of the medium, pump beam heating decreases the refractive index mismatch and the resulting diffraction.

#### 4. Conclusions

We have observed for the first time optical switching in the 3 nsec time regime from an absorbing crystalline colloidal array, as previously theoretically predicted.<sup>11</sup> We are continuing to optimize these materials for optoelectronic applications.

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